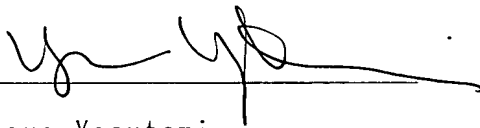


VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of Chuo BLDG., 4-20, Nishinakajima 5-chome,  
Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN, hereby declare that I am  
conversant with the Japanese and English languages and that I am the  
translator of the documents attached and certify that to the best of  
my knowledge and belief the following is a true and correct English  
translation of the Japanese Patent Application No. Hei 10-234428  
in the name of KANEKA CORPORATION.

Dated this *6th* day of *August*, 2004

  
\_\_\_\_\_  
Yasuo Yasutomi

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[Title of the Invention] POLYMER AND USE

[Number of Claims] 23

[Inventor]

[Address or Residence] c/o Kobe Research Laboratories Research  
Institute of Kaneka Corporation  
2-80, Yoshidacho 1-chome, Hyogo-ku,  
Kobe-shi, HYOGO

[Name] NAKAGAWA Yoshiki

[Inventor]

[Address or Residence] c/o Kobe Research Laboratories Research  
Institute of Kaneka Corporation  
2-80, Yoshidacho 1-chome, Hyogo-ku,  
Kobe-shi, HYOGO

[Name] FUJITA Masayuki

[Applicant]

[Identification Number] 000000941

[Name] KANEKA CORPORATION

[Representative] FURUTA Takeshi

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[List of Attached Documents]

[Document Name]	Description	1
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[Document Name]	Abstract	1
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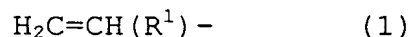
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[Document Name] Description

[Title of the Invention] POLYMER AND USE

[Scope of Claims for Patent]

[Claim 1] A block copolymer which is produced by adding a  
5 polymer (I) containing at least one group represented by the  
general formula 1:



(wherein  $\text{R}^1$  represents a hydrogen atom or a hydrocarbon group  
containing 1 to 20 carbon atoms) to a living radical  
10 polymerization system.

[Claim 2] The polymer according to Claim 1, wherein, in the  
general formula 1,  $\text{R}^1$  is a hydrogen atom.

[Claim 3] The polymer according to Claim 1 or 2, wherein the  
polymer (I) has at least one group represented by the general  
15 formula 1 at its terminus.

[Claim 4] The polymer according to any of Claims 1 to 3,  
wherein the polymer (I) is a polyester polymer.

[Claim 5] The polymer according to any of Claims 1 to 3,  
wherein the polymer (I) is a polyether polymer.

20 [Claim 6] The polymer according to any of Claims 1 to 3,  
wherein the polymer (I) is a vinyl polymer.

[Claim 7] The polymer according to any of Claims 1 to 3,  
wherein the polymer (I) is a (meth)acrylic polymer.

[Claim 8] The polymer according to any of Claims 1 to 3,  
25 wherein the polymer (I) is a polysiloxane polymer.

[Claim 9] The polymer according to any of Claims 1 to 3,  
wherein the polymer (I) is a hydrocarbon polymer.

[Claim 10] The polymer according to any of Claims 1 to 9,  
wherein the polymer (I) has a plurality of the groups  
30 represented by the general formula 1.

[Claim 11] The polymer according to any of Claims 1 to 10,  
wherein the polymer (I) has one group represented by the general  
formula 1.

[Claim 12] The polymer according to any of Claims 1 to 11,  
35 wherein the polymer (I) has the number average molecular weight

of 500 to 100000.

[Claim 13] The polymer according to any of Claims 1 to 12, wherein the polymer (I) has the ratio between the weight average molecular weight (Mw) and the number average molecular weight (Mn) (Mw/Mn) as determined by gel permeation chromatography of less than 1.8.

[Claim 14] The polymer according to any of Claims 1 to 13, wherein a polymer chain produced by living radical polymerization comprising adding the polymer (I) has a glass transition point not higher than 25°C.

[Claim 15] The polymer according to any of Claims 1 to 14, wherein a polymer produced by living radical polymerization comprising adding the polymer (I) is a styrenec polymer.

[Claim 16] The polymer according to any of Claims 1 to 15, wherein the polymer produced by living radical polymerization comprising adding the polymer (I) is a (meth)acrylic polymer.

[Claim 17] The polymer according to any of Claims 1 to 16, wherein the living radical polymerization comprising adding the polymer (I) is an atom transfer radical polymerization.

[Claim 18] The polymer according to Claim 17, wherein the metal complex to serve as a catalyst for the atom transfer radical polymerization is a copper, nickel, ruthenium or iron complex.

[Claim 19] The polymer according to Claim 18, wherein the metal complex to serve as a catalyst for the atom transfer radical polymerization is a copper complex.

[Claim 20] The polymer according to Claims 1 to 19, wherein the living radical polymerization comprising adding the polymer (I) is started by a di- or more functional initiator.

[Claim 21] The polymer according to any of Claims 1 to 20, wherein the ratio between the weight average molecular weight (Mw) and the number average molecular weight (Mn) (Mw/Mn) as determined by gel permeation chromatography of not more than 1.8.

[Claim 22] A thermoplastic elastomer which contains the

polymer according to any of Claims 1 to 21.

[Claim 23] An impact resistance improving agent which contains the polymer according to any of Claims 1 to 21.

[Detailed Description of the Invention]

5 [0001]

[Technical Field of the Invention]

The present invention relates to a method of producing a block copolymer which comprises adding various alkenyl-terminated polymers to a living radical polymerization system, the polymer, and its use.

10 [0002]

[Prior Art]

Block copolymers composed of different polymer block species bound to each other are generally produced by polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block copolymers using them. When cationic polymerization is employed, however, it is difficult to control the polymerization, since the growing species carbenium ion is unstable. In recent years, examples of the so-called living cation polymerization in which the growing carbenium ion in the cationic polymerization is inhibited from undergoing isomerization, chain transfer reaction or termination reaction have been reported. For example, Higashimura et al. (Macromolecules, 17, 265, 1984) report that cationic living polymerization is possible in vinyl ether polymerization using a combination of hydrogen iodide and iodine as an initiator. However, the polymerization using such initiator has various problems; for instance, its application is restricted to those monomers which have an alkoxy group high in electron donating ability and are highly susceptible to cationic polymerization, and the initiator is unstable and difficult to handle.

25 [0003]

35 On the other hand, Kennedy et al. (Japanese Kokai

Publication Sho-62-48704, Japanese Kokai Publication Sho-64-62308), by polymerizing olefin monomers, such as isobutylene, using an organic carboxylic acid or an ester, or an ether as an initiator in combination with a Lewis acid, showed  
5 that cationic living polymerization is possible with olefin monomers as well. This method has been modified in several ways, and Nippon Zeon (Japanese Kokoku Publication Hei-07-59601) has succeeded in obtaining block copolymers by successive monomer addition with additional use of an amine. In this modification,  
10 isobutylene-based block copolymers comprising an isobutylene polymer and a styrene polymer are produced in an mixed solvent composed of methylene chloride and hexane. However, such halogenated hydrocarbons containing 1 or 2 carbon atoms have problems; for instance, they are difficult to handle, and  
15 require large scale equipment for preventing them from being discharged into the environment to raise the cost of production. Although, on the other hand, such polymerization is also possible in a halogen-free solvent such as toluene, very fine adjustment is required, depending on the monomer, for the  
20 monomer to show adequate polarity. It is thus very difficult to establish the conditions for successive polymerization of two or more monomer species differing in reactivity.  
[0004]

Furthermore, in recent years, controlled radical  
25 polymerization techniques and, further, living radical polymerization techniques have been developed, making it possible to well control the living polymerization. Matyjaszewski et al. report a method of synthesizing block copolymers by successively adding monomers using the atom  
30 transfer radical polymerization technique to be mentioned later herein or by using a macro-initiator. These techniques, however, may sometimes encounter problems; successive polymerization of monomers is difficult since respective monomers require different optimum polymerization conditions,  
35 or it is difficult to introduce, terminally into the

macro-initiator, an initiator terminus optimal to the next monomer to be polymerized.

[0005]

Meanwhile, a further method available for the production of block copolymers comprises synthesizing respective polymer blocks individually and then coupling them to each other. In that case, however, it is not easy to accomplish the coupling reaction quantitatively and selectively. Thus, very few methods have been found that are commercially advantageous.

10 [0006]

[Subject which the Invention is to Solve]

The present invention has for its object to provide a method for easily producing a block copolymer composed of any of various polymers and a living radical polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[0007]

[Means for Solving the Problems]

The present invention relates to a block copolymer which is produced by adding a polymer (I) containing at least one group represented by the general formula 1:



(wherein  $\text{R}^1$  represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) to a living radical polymerization system.

25 [0008]

The polymer block copolymer and the respective polymer blocks of the present invention also have a characteristic for having a narrow molecular weight distribution.

30 The main chain of the polymer (I) is not particularly restricted, but is preferably a polyester polymer, polyether polymer, vinyl polymer, (meth)acrylic polymer, polysiloxane polymer and hydrocarbon polymer.

[0009]

35 The living radical polymerization to which the polymer

(I) is added is not particularly restricted, but preferred is an atom transfer radical polymerization system.

The block copolymer of the present invention is useful as a thermoplastic elastomer or an impact resistance improving agent.

[0010]

[Embodiment of the Invention]

The present invention relates to a block copolymer which is produced by adding the polymer (I) containing at least one group represented by the general formula 1:



to a living radical polymerization system.

#### Description of polymer (I)

In the general formula 1,  $\text{R}^1$  is a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:

-  $(\text{CH}_2)_n-\text{CH}_3$ , - $\text{CH}(\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$ , - $\text{CH}(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$ ,  
 - $\text{CH}(\text{CH}_2\text{CH}_3)_2$ , - $\text{C}(\text{CH}_3)_2-(\text{CH}_2)_n-\text{CH}_3$ , - $\text{C}(\text{CH}_3)(\text{CH}_2\text{CH}_3)-(\text{CH}_2)_n-\text{CH}_3$ ,  
 - $\text{C}_6\text{H}_5$ , - $\text{C}_6\text{H}_5(\text{CH}_3)$ , - $\text{C}_6\text{H}_5(\text{CH}_3)_2$ , - $(\text{CH}_2)_n-\text{C}_6\text{H}_5$ , - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)$ ,  
 - $(\text{CH}_2)_n-\text{C}_6\text{H}_5(\text{CH}_3)_2$

(wherein  $n$  is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

[0011]

The mode of bonding between the group represented by the general formula 1 and the main chain of the polymer is not particularly restricted but is preferably of the carbon-carbon, ester, ester, carbonate, amide, urethane or like bonding type.

The position of the group represented by the general formula 1 in polymer (I) is not particularly restricted but may be at the terminus or in the middle of the main chain. In accordance with the present invention, straight-chain block copolymers can be synthesized when said group is at the terminus and, when it is in the middle of the main chain, branched block copolymers ramifying from that site can be synthesized.



[0012]

The number of the groups represented by the general formula 1 in polymer (I) is not particularly restricted but may be selected depending on the structure of the desired block copolymer. Thus, said polymer may have one, two or more alkenyl groups.

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the polymer (I) of the present invention is not particularly restricted but is preferably less than 1.8, more preferably not more than 1.7, still more preferably not more than 1.6, much more preferably not more than 1.5, in particular not more than 1.4, most preferably not more than 1.3. In the practice of the present invention, the number average molecular weight can be determined by GPC generally using chloroform as mobile phase and a polystyrene gel column and thus it can be expressed in terms of polystyrene equivalent.

[0013]

The number average molecular weight of the vinyl polymer of the present invention is not particularly restricted but is preferably within the range of 500 to 1,000,000, more preferably within the range of 1,000 to 100,000.

<Method of polymerizing the polymer (I)>

The polymerization method for producing the polymer (I) is not particularly restricted. Said polymer can be synthesized by various techniques of polymerization such as anionic polymerization, cationic polymerization, radical polymerization, coordination polymerization, group transfer polymerization, condensation polymerization and ring opening polymerization. Among them, living polymerization, such as living anionic polymerization, living cationic polymerization and living radical polymerization, are preferred since it is preferred that the molecular weight and molecular weight distribution be controlled.

<Main chain of polymer (I)>

The main chain of polymer (I) according to the present invention is not particularly restricted but includes polyester polymers, polyether polymers, vinyl polymers, (meth)acrylic  
 5 polymers, polysiloxane polymers, hydrocarbon polymers, polycarbonate polymers, polyarylate polymers, diallyl phthalate polymers, polyamide polymers and polyimide polymers, among others.

<Terminal functional group introduction>

10 As for the method of introducing the group represented by the general formula 1 into the polymer, various methods that have so far been proposed can be used. These methods can be roughly classified into two groups; in one group, the alkenyl group introduction is carried out after polymerization and, in  
 15 the other, the alkenyl group introduction is carried out during polymerization. In cases where the alkenyl group introduction is effected after polymerization, an alkenyl group can be introduced, for example, into a terminus, the main chain or a side chain of an organic polymer having a functional group, such  
 20 as a hydroxyl or alkoxide group, at a terminus, in the main chain or in a side chain by reacting said polymer with an organic alkenyl-containing compound having an active group reactive with said functional group. As examples of said organic alkenyl-containing compound having an active group reactive  
 25 with the above-mentioned functional group, there may be mentioned unsaturated fatty acids having 3 to 20 carbon atoms, acid halides, acid anhydrides, such as acrylic acid, methacrylic acid, vinylacetic acid, acryloyl chloride and acryloyl bromide; unsaturated fatty acid-substituted carbonic  
 30 acid halides having 3 to 20 carbon atoms such as allyl chloroformate ( $\text{CH}_2=\text{CHCH}_2\text{OCOC}\text{l}$ ) and allyl bromoformate ( $\text{CH}_2=\text{CHCH}_2\text{OCOB}\text{r}$ ); allyl chloride, allyl bromide, vinyl(chloromethyl)benzene, allyl(chloromethyl)benzene, vinyl(bromomethyl)benzene, allyl(bromomethyl)benzene, allyl  
 35 chloromethyl ether, allyl(chloromethoxy)benzene, 1-butenyl

chloromethyl ether, 1-hexenyl(chloromethoxy)benzene, allyloxy(chloromethyl)benzene and the like.

[0014]

For effecting alkenyl group introduction during polymerization, alkenyl group introduction into the main chain of a polymer or at a terminus thereof can be realized, for example, by using, in the polymerization by radical polymerization, a vinyl monomer having an alkenyl group low in radical reactivity in the molecule, such as allyl methacrylate or allyl acrylate, or a radical chain transfer agent having an alkenyl group low in radical reactivity such as allyl mercaptan.

#### Production of a block copolymer

In the present invention, a block copolymer is produced by adding the above-mentioned polymer (I) to a living radical polymerization system.

In the following, the living radical polymerization is described.

#### <Living radical polymerization>

In its narrow sense, the term "living polymerization" means that polymerization in which the molecular chain grows while a terminus always retain activity. Generally, however, it also includes, within the meaning thereof, pseudoliving polymerization in which molecules grow while terminally inactivated molecules and terminally activated ones are in equilibrium. The latter definition is to be applied to the present invention. "Living radical polymerization" has recently been aggressively investigated by a number of groups. As examples, there may be mentioned, among others, the method which uses cobalt porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and atom transfer radical polymerization (ATRP) in which an organic halide, for instance, is used as an initiator and a transition metal complex as a catalyst. The living radical polymerization hardly

undergo termination reaction and give polymers narrow in molecular weight distribution ( $M_w/M_n$  being about 1.1 to 1.5) and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization regarded as difficult to control because of a high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other, among others.

[0015]

10 "Living radical polymerization methods", which enable introduction of a specific functional group-containing monomer into a polymer at a substantially arbitrary site thereof in addition to obtaining polymers with a narrow molecular weight distribution and a low viscosity on its properties, are more preferred as methods of producing the specific functional group-containing vinyl polymers.

Among such "living radical polymerization methods", the "atom transfer polymerization methods" for polymerizing vinyl monomers using an organic halide, sulfonyl halide or the like as an initiator and a transition metal complex as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614; Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721) are more preferred as the method of producing specific functional group-containing vinyl polymers, since, in addition to the characteristic features of the above-mentioned "living radical polymerization methods", halogen, etc., relatively favorable for functional group conversion reactions is contained at its terminus and the degree of freedom is high in designing the initiator or catalyst. Also in the method of the present invention, the atom transfer polymerization method is preferred.

[0016]

35 In this atom transfer radical polymerization, an organic

halide, in particular an organic halide having a highly reactive carbon-halogen bond (e.g. a carbonyl compound having a halogen in  $\alpha$ -position or a compound having a halogen at the benzyl site), or a sulfonyl halide compound is used as an initiator.

5 <Monomer>

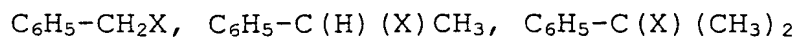
The vinyl monomer used in the living radical polymerization of the present invention is not particularly restricted, and various ones may be used. Examples are (meth)acrylic monomers such as (meth)acrylic acid, methyl  
 10 (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl  
 15 (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate,  
 20 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate,  $\gamma$ -(methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate,  
 25 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate,  
 30 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene,  $\alpha$ -methylstyrene, chlorostyrene, styrenesulfonic acid and salts thereof; fluorine-containing vinyl monomers such as  
 35 perfluoroethylene, perfluoropropylene and vinylidene

fluoride; silicon-containing vinyl monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and dialkyl esters; maleimide monomers such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amide group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products. More preferred are acrylic acid ester monomers and methacrylic acid ester monomers, and still more preferred are butyl acrylate monomers. In the practice of the present invention, such a preferred monomer may be copolymerized with some other monomers and, on that occasion, the content of such preferred monomer is preferably 40% on the weight basis. The term (meth)acrylic acid employed hereinabove means acrylic acid and/or methacrylic acid.

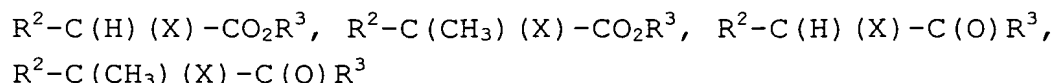
[0017]

<Initiator of atom transfer radical polymerization>

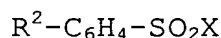
The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, among others:



(in the above chemical formulas,  $\text{C}_6\text{H}_5$  is a phenyl group and X is chlorine, bromine or iodine);



(in which  $R^2$  represents a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, X is chlorine, bromine or iodine, and  $R^3$  represents a monovalent organic group having 1 to 20 carbon atoms); and



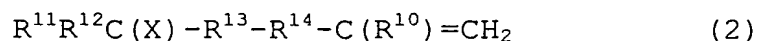
(in which  $R^2$  is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or aralkyl group having 7 to 20 carbon atoms and X is chlorine, bromine or iodine).

[0018]

Furthermore, when an organic halide or sulfonyl halide having a functional group other than the functional group for initiating polymerization is used as the initiator, a polymer introduced with a functional group at its terminus can be easily obtained. As such functional group, there may be mentioned alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among others. By introducing the group represented by the general formula 1 to the polymer produced from an initiator containing such functional groups by various methods described later to produce the polymer (I), and adding the polymer to the living radical polymerization system, a block copolymer containing various functional groups at its terminus can be easily obtained.

[0019]

The alkenyl-containing organic halide is not restricted but may be one having the structure shown by the general formula 2:



(wherein  $R^{10}$  is a hydrogen atom or a methyl group,  $R^{11}$  and  $R^{12}$  each is a hydrogen atom or a monovalent alkyl having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group and  $R^{11}$  and  $R^{12}$  may be bound to each other at

respective other termini,  $R^{13}$  is  $-C(O)O-$  (ester group),  $-C(O)-$  (keto group) or an o-, m- or p-phenylene group,  $R^{14}$  is a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally contain one or more ether bonds, and X is  
 5 chlorine, bromine or iodine).

In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization is started after the carbon-halogen bond is activated.

[0020]

10 As specific examples of the substituents  $R^{11}$  and  $R^{12}$ , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc.  $R^{11}$  and  $R^{12}$  may be bound to each other at respective other termini to form a cyclic skeleton. In such case,  $-R^{11}-R^{12}-$  may be, for example,  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  
 15  $-CH_2CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2CH_2-$  and the like.

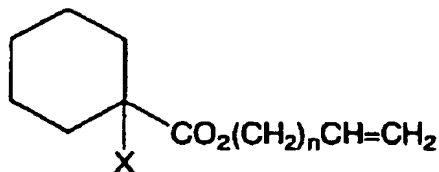
[0021]

As specific examples of the alkenyl-containing organic halide represented by the general formula 2, there may be mentioned the following:

20  $XCH_2C(O)O(CH_2)_nCH=CH_2$ ,  
 $H_3CC(H)(X)C(O)O(CH_2)_nCH=CH_2$ ,  
 $(H_3C)_2C(X)C(O)O(CH_2)_nCH=CH_2$ ,  
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nCH=CH_2$

[0022]

25 [Chemical 1]

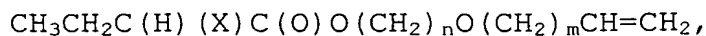


30 [0023]

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

$XCH_2C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$ ,  
 $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$ ,  
 35  $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mCH=CH_2$ ,

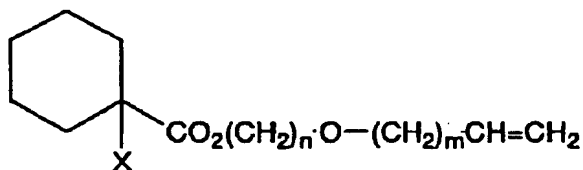




[0024]

[Chemical 2]

5



[0025]

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

o,m,p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>,

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

o,m,p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>,

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20);

o,m,p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-CH=CH<sub>2</sub>,

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20);

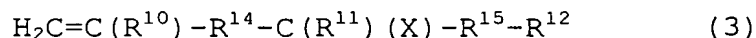
o,m,p-XCH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>,

o,m,p-CH<sub>3</sub>CH<sub>2</sub>C(H)(X)-C<sub>6</sub>H<sub>4</sub>-O-(CH<sub>2</sub>)<sub>n</sub>-O-(CH<sub>2</sub>)<sub>m</sub>-CH=CH<sub>2</sub>,

(in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20 and m is an integer of 0 to 20).

As the alkenyl-containing organic halide, there may further be mentioned compounds represented by the general formula 3:



(wherein R<sup>10</sup>, R<sup>11</sup>, R<sup>12</sup>, R<sup>14</sup> and X are defined above and R<sup>15</sup> is a

direct bond,  $-\text{C}(\text{O})\text{O}-$  (ester group),  $-\text{C}(\text{O})-$  (keto group) or an o-, m- or p-phenylene group).

$\text{R}^{24}$  is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain one or more ether bonds) and, when it is a direct bond, the vinyl group is bound to the carbon to which the halogen is bound, to form an allyl halide. In this case, the carbon-halogen bond is activated by the neighboring vinyl group, so that it is not always necessary for  $\text{R}^{15}$  to be a  $\text{C}(\text{O})\text{O}$  group or a phenylene group, for instance, but it may be a direct bond. When  $\text{R}^{14}$  is not a direct bond,  $\text{R}^{15}$  is preferably a  $\text{C}(\text{O})\text{O}$  group,  $\text{C}(\text{O})$  group or phenylene group so that the carbon-halogen bond may be activated.

[0026]

As a specific example of compounds represented by the general formula 3, there can be mentioned,

$\text{CH}_2=\text{CHCH}_2\text{X}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{X}$ ,  
 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}_3$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{H})(\text{X})\text{CH}_3$ ,  
 $\text{CH}_2=\text{CHC}(\text{X})(\text{CH}_3)_2$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{C}_2\text{H}_5$ ,  
 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}(\text{CH}_3)_2$ ,  
 $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CHC}(\text{H})(\text{X})\text{CH}_2\text{C}_6\text{H}_5$ ,  
 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CHCH}_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,

(in the above formulas, X is chlorine, bromine or iodine, and R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms). Among these, allyl chloride and allyl bromide are preferred from cost and availability viewpoint.

[0027]

Specific examples of the alkenyl-containing sulfonyl halide are as follows:

o-, m- or p-CH<sub>2</sub>=CH-(CH<sub>2</sub>)<sub>n</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>X and

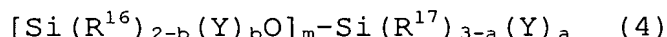
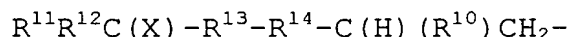
o-, m- or p-CH<sub>2</sub>=CH-(CH<sub>2</sub>)<sub>n</sub>-O-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>X

(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20), among others.

5 [0028]

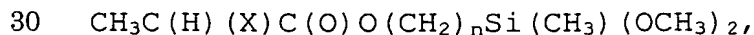
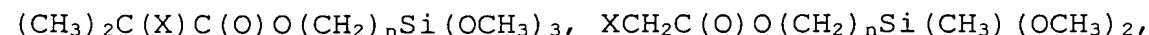
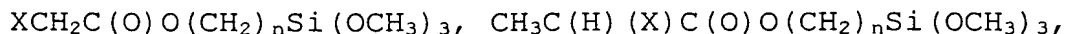
When an alkenyl-containing initiator is used, care should be taken since there is a possibility that olefin of the initiator may also react with the polymerization terminus.

The crosslinking silyl-containing organic halide is not particularly restricted but includes, among others, those having a structure shown by the general formula 4:

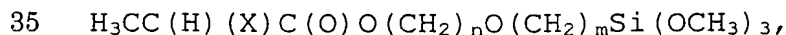
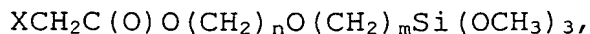


(wherein R<sup>10</sup>, R<sup>11</sup>, R<sup>12</sup>, R<sup>13</sup>, R<sup>14</sup> and X are as defined above, R<sup>16</sup> and R<sup>17</sup> each is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, or a triorganosiloxy group represented by (R')<sub>3</sub>SiO- (in which R' is a monovalent hydrocarbon group having 1 to 20 carbon atoms and the three R' groups may be the same or different) and, when there are two or more R<sup>16</sup> and/or R<sup>17</sup> groups, they may be the same or different, Y represents a hydroxyl group or a hydrolyzable group and, when there are two or more Y groups, they may be the same or different, a represents 0, 1, 2 or 3, b represents 0, 1 or 2 and m is an integer of 0 to 19, provided that the relation a+mb ≥ 1 should be satisfied.

As a specific example of compounds represented by the general formula 4, there can be mentioned,

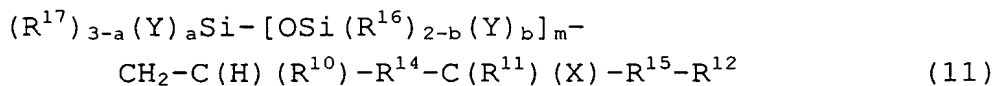


(wherein, in each formula, X is chlorine, bromine or iodine and n is an integer of 0 to 20),



- $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$   
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{OCH}_3)_3,$   
 $\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$   
 $\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$   
 5  $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$   
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{Si}(\text{CH}_3)(\text{OCH}_3)_2,$   
 (wherein, in each formula, X is chlorine, bromine or iodine,  
 n is an integer of 0 to 20, and m is an integer of 0 to 20),  
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si(OCH}_3)_3,$   
 10  $\text{o, m, p-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2)_2\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 15  $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 20  $\text{o, m, p-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-XCH}_2\text{-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 $\text{o, m, p-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-O-(CH}_2)_2\text{-O-(CH}_2)_3\text{Si(OCH}_3)_3,$   
 (wherein, in each formula, X is chlorine, bromine or iodine).

- 25 As further examples of the crosslinking silyl-containing organic halide, there may be mentioned those having a structure represented by the general formula 5:



- 30 (wherein  $\text{R}^{10}$ ,  $\text{R}^{11}$ ,  $\text{R}^{12}$ ,  $\text{R}^{14}$ ,  $\text{R}^{15}$ ,  $\text{R}^{16}$ ,  $\text{R}^{17}$ , a, b, m, X and Y are as defined above).

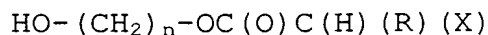
As a specific example of such compounds, there can be mentioned;

- $(\text{CH}_3\text{O})_3\text{SiCH}_2\text{CH}_2\text{C(H)(X)C}_6\text{H}_5,$   $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{SiCH}_2\text{CH}_2\text{C(H)(X)C}_6\text{H}_5,$   
 35  $(\text{CH}_3\text{O})_3\text{Si(CH}_2)_2\text{C(H)(X)-CO}_2\text{R},$   $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si(CH}_2)_2\text{C(H)(X)-CO}_2\text{R},$

$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_9\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_9\text{C}(\text{H})(\text{X})-\text{CO}_2\text{R}$ ,  
 $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  
 5  $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  $(\text{CH}_3\text{O})_2(\text{CH}_3)\text{Si}(\text{CH}_2)_4\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_5$ ,  
 (wherein, in each formula, X is chlorine, bromine or iodine, R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms.), and the like.

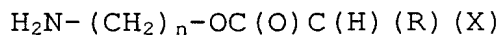
10 [0029]

The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



15 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

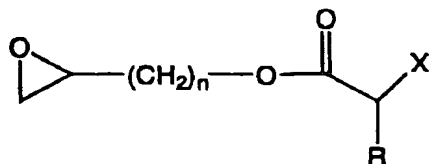


20 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The above-mentioned epoxy-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

30 [0030]

[Chemical 3]



35

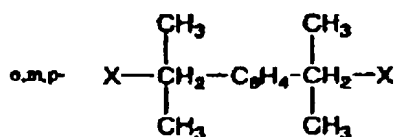
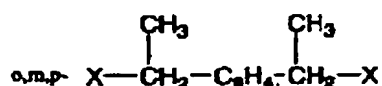
[0031]

(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 5 20 carbon atoms and n is an integer of 1 to 20).

An organic halide or sulfonyl halide having two or more initiation sites is used as an initiator. Specific examples are:

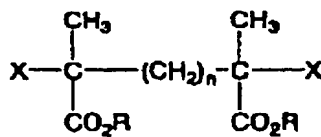
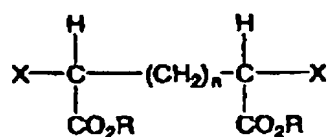
[0032]

10 [Chemical 4]

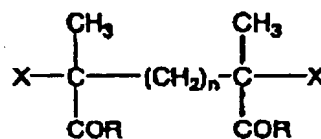
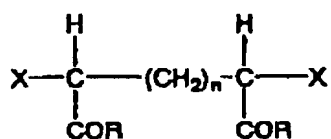


15

(in which  $C_6H_4$  represents a phenylene group and X is chlorine, bromine or iodine);



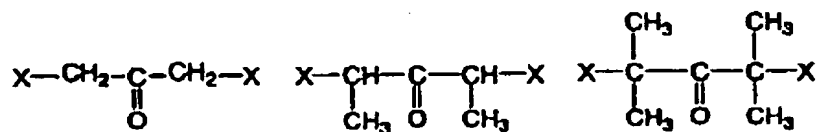
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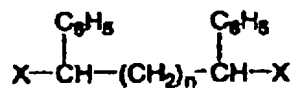
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(in which R is an alkyl group having 1 to 20 carbon atoms, aryl or aralkyl group, n is an integer of 0 to 20 and X is chlorine, 30 bromine or iodine);

35



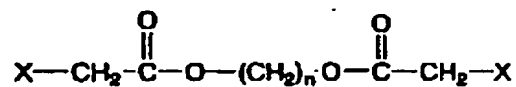
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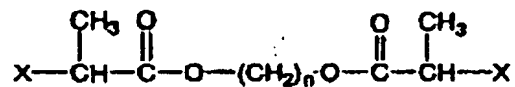
(in which X is chlorine, bromine or iodine and n is an integer of 0 to 20);

10 [0033]

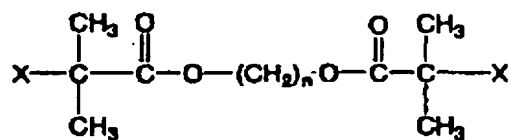
[Chemical 5]



15



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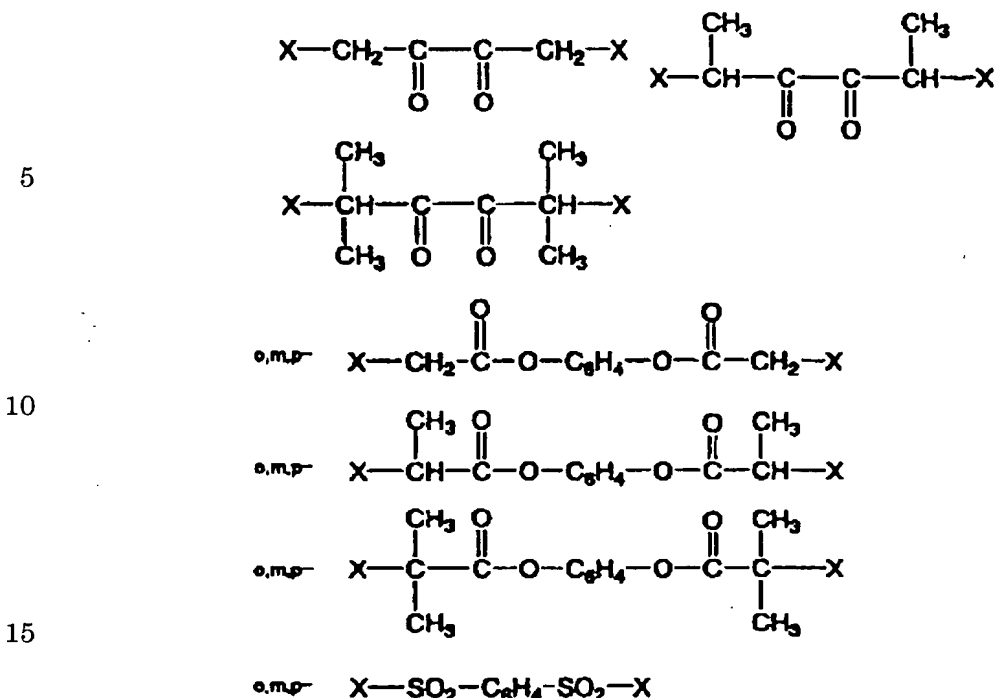


(in which n is an integer of 0 to 20 and X is chlorine, bromine or iodine);

25

30

35



(in which X is chlorine, bromine or iodine), and the like.  
[0034]

#### 20 <Catalyst of atom radical polymerization>

The transition metal complex to be used as a polymerization catalyst for the atom transfer radical polymerization is not particularly restricted but preferably is a metal complex containing an element of the group 7, 8, 9, 10 or 11 of the periodic table as a central metal, and more preferably are complexes of monovalent copper, copper (valence: zero), divalent ruthenium, divalent iron or divalent nickel. Among them, copper complexes are preferred in view of cost and reaction controllability. Specific examples of monovalent copper compounds are cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide, cuprous perchlorate and the like. When a copper compound is used, a ligand, such as 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof or a polyamine such as tetramethylethylenetriamine (TMEDA),



pentamethyldiethylenetriamine or hexamethyl  
 (2-aminoethyl)amine, is added to enhance the catalytic activity.  
 A tris(triphenylphosphine) complex of divalent ruthenium  
 chloride ( $\text{RuCl}_2(\text{PPh}_3)_3$ ) is also suited for use as a catalyst.  
 5 When a ruthenium compound is used as a catalyst, an aluminum  
 alkoxide is added as an activator. Furthermore, a  
 bis(triphenylphosphine) complex of divalent iron ( $\text{FeCl}_2(\text{PPh}_3)_2$ );  
 a bis(triphenylphosphine) complex of divalent nickel  
 ( $\text{NiCl}_2(\text{PPh}_3)_2$ ) and a bis(tributylphosphine) complex of divalent  
 10 nickel ( $\text{NiBr}_2(\text{PBu}_3)_2$ ) are also suited as catalysts.

<Solvent and temperature of living radical polymerization>

The above-mentioned living radical polymerization, and  
 further atom transfer radical polymerization can be carried out  
 in the absence or presence of various solvents. As the solvent,  
 15 there may be mentioned, among others, hydrocarbon solvents such  
 as benzene and toluene; ether solvents such as diethyl ether  
 and tetrahydrofuran; halogenated hydrocarbon solvents such as  
 methylene chloride and chloroform; ketone solvents such as  
 acetone, methyl ethyl ketone and methyl isobutyl ketone;  
 20 alcohol solvents such as methanol, ethanol, propanol,  
 isopropanol, n-butyl alcohol and tert-butyl alcohol; nitrile  
 solvents such as acetonitrile, propionitrile and benzonitrile;  
 ester solvents such as ethyl acetate and butyl acetate; and  
 carbonate solvents such as ethylene carbonate and propylene  
 25 carbonate. These may be used singly or two or more of them may  
 be used in admixture. The above polymerization can be conducted  
 within the temperature range of room temperature to  $200^\circ\text{C}$ ,  
 preferably  $50^\circ\text{C}$  to  $150^\circ\text{C}$ .

<Addition of polymer (I)>

30 The time for adding the polymer (I) to the living radical  
 polymerization system is not particularly restricted but is  
 preferably in the terminal stage of polymerization. The amount  
 of the polymer (I) to be added is not particularly restricted  
 but is preferably such that the number of growing termini in  
 35 living radical polymerization be equal to the number of the

terminus represented by the general formula 1 in polymer (I).  
[0035]

The polymer (I) may be added as such or in the form of a solution in a solvent which will not adversely affect the living radical polymerization.

Structure of the block copolymer

The structure of the block copolymer of the present invention is not particularly restricted but includes those copolymers classifiable on the basis of polymer (I) and of the system to which the polymer (I) is added, namely living radical polymerization, as follows:

(1) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per molecule and a unifunctional initiator; (2) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per molecule and a bifunctional initiator; (3) living radical polymerization using a polymer (I) having one group represented by the general formula 1 per molecule and a polyfunctional initiator; (4) living radical polymerization using a polymer (I) having two groups represented by the general formula 1 per molecule and a unifunctional initiator; (5) living radical polymerization using a polymer (I) having more than two groups represented by the general formula 1 per molecule and a unifunctional initiator; (6) living radical polymerization using a polymer (I) having two groups represented by the general formula 1 per molecule and a bifunctional initiator; (7) the case in which either of the number of the group represented by the general formula 1 and the number of initiation sites of the initiator in living radical polymerization is not less than 2 and the other is not less than 3; and so forth.

In the case of (1), an AB type block copolymer is obtained; in the case of (2) or (4), an ABA type block copolymer is obtained; in the case of (3) or (5), a stellar block copolymer is obtained; in the case of (6), a multiblock copolymer is

obtained; and in the case of (7), a crosslinked block copolymer is obtained.

[0036]

For each polymer block, various species can be synthesized. In an ABA type block copolymer, for instance, when  
5 A is a polymer having a higher glass transition point (not specifically restricted but, for example, not lower than 25°C) and B is a polymer having a lower glass transition point (not specifically restricted but, for example, not higher than 25°C),  
10 properties as a thermoplastic elastomer can be expected. In the case of stellar polymers as well, properties as a thermoplastic elastomer can be expected when a polymer block having a higher glass transition point is used as the exterior block and a polymer block having a lower glass transition point  
15 as the inside block.

[0037]

Accordingly, by the present invention, block copolymers in which various species of blocks are combined in various orders can be obtained, and can be used in various fields such  
20 as thermoplastic elastomers and impact resistance improving agents.

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the  
25 block copolymer of the present invention is not particularly restricted but is preferably less than 1.8, more preferably not more than 1.7, still more preferably not more than 1.6, much more preferably not more than 1.5, in particular not more than 1.4, most preferably not more than 1.3. In the practice of the  
30 present invention, the number average molecular weight can be determined by GPC generally using chloroform as mobile phase and a polystyrene gel column and thus it can be expressed in terms of polystyrene equivalent.

#### Uses

35 <Thermoplastic elastomer>

The block copolymer obtained by the production method of the present invention can be used in substantially the same fields of application as the existing thermoplastic elastomers. More specifically, it can be used for modifying resins or asphalt, for preparing compounds of the block copolymer with resins (with a plasticizer, a filler, a stabilizer, etc. added as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be mentioned automotive upholstery and exterior, electric and electronic fields, food wrapping films and tubes, drug containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

While the block copolymer obtained by the production method of the present invention by itself can serve as a molding material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a high level of impact resistance when admixed with said resins. Further, it can also be used as a processability improving agent, compatibilizing agent, flattening agent, heat resistance modifier or the like. Furthermore, improvement of gas barrier property based on an isobutylene polymer can be expected.

[0038]

The thermoplastic resins which can be improved in shock resistance by addition of the block copolymer of the present invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins, polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic alkenyl compounds, vinyl cyanide compounds and (meth)acrylic

acid esters and 0 to 30% by weight of another vinyl monomer copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene ether resins, polystyrene-polyphenylene ether resin blends and the like. Said block copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and polyester resins, among others, are preferred since they can readily show its characteristics such as improved weathering resistance and impact resistance.

[0039]

As the method of adding the block copolymer of the present invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an ordinary injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0040]

Furthermore, in the resulting resin compositions, there may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), acrylic graft copolymers and acrylic-silicone composite rubber type graft copolymers; stabilizers such as triphenyl phosphite; lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire retardants, e.g. decarbromobiphenyl, decabromodiphenyl ether,

and antimony trioxide; pigments such as titanium oxide, zinc sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0041]

5 [Examples]

In the following, specific examples of the present invention are described. The following examples, however, are by no means limitative of the scope of the present invention. In the GPC measurement in Examples, a polystyrene gel column  
10 was used while using chloroform as mobile phase, and the values of the molecular weight was expressed in terms of polystyrene equivalent.

(Production Example 1)

According to the method disclosed in Japanese Kokai  
15 Publication Sho-53-134095, an allyl type olefin-terminated polyoxypropylene was synthesized.

[0042]

Thus, polyoxypropylene glycol with an average molecular weight of 3,000 and powdery caustic soda were stirred at 60°C,  
20 then bromochloromethane was added, and the reaction was allowed to proceed to increase the molecular weight. Then, allyl chloride was added, and terminal allyl etherification was carried out at 110°C. Terminally allyl-etherified polyoxypropylene in purified form was synthesized by treating  
25 the reaction product with aluminum silicate.

[0043]

This polyether had a average molecular weight of 7,960 and, based on the iodine value, 92% of the termini were occupied by the olefinic group (0.0231 mol/100 g). The viscosity was  
30 130 poises (40°C) as measured using a type E viscometer.

(Production Example 2)

A one-liter four-necked flask equipped with stirrer, dropping funnel, thermometer, three-way cock and condenser was prepared and charged with 300 g of hydroxyl-terminated  
35 polytetramethylene oxide with an average molecular weight of

about 2,000 (trademark: Terathane-2000; product of du Pont). After azeotropic degassing using toluene, a solution of 50.5 g of t-BuOK in 200 mL of THF was added. After 1 hour of stirring at 50°C, 49 mL of allyl chloride was added dropwise from the dropping funnel over 1 hour. After completion of the dropping, the reaction was allowed to proceed at 50°C for about 1 hour. Then, 30 g of aluminum silicate was added at room temperature and the mixture was stirred for 30 minutes. Said mixture was filtered using diatomaceous earth as filtration aid, and the volatile components were removed using an evaporator, whereupon about 230 g of a transparent viscous liquid was obtained. This product was allowed to stand overnight at room temperature, whereupon it crystallized and became a white solid. Iodometry (0.0718 mol/100 g) revealed that the allyl group had been introduced into this polytetramethylene oxide at about 73% of the termini thereof.

(Production Example 3)

Toluene (50 mL) was added to 300 g of hydrogenated polyisoprene having a hydroxyl group at both termini (product of Idemitsu Petrochemical; trademark: Epol), and the mixture was dehydrated by azeotropic degassing. A solution of 48 g of t-BuOK in 200 mL of THF was injected into the mixture. After 1 hour of reaction at 50°C, 47 mL of allyl chloride was added dropwise over about 30 minutes. After completion of the dropping, the reaction was allowed to proceed at 50°C for 1 hour. Thereafter, for the adsorption of the product salt, 30 g of aluminum silicate was added to the reaction mixture and the whole mixture was stirred at room temperature for 30 minutes. Purification by filtration gave about 250 g of allyl-terminated hydrogenated polyisoprene as a viscous liquid. 300 MHz 1H NMR analysis confirmed the allyl group introduction at 92% of the termini. The number of moles of the olefin as determined based on the iodine value was 0.1046 mol/100 g. The viscosity was 302 poises (23°C) as measured using a type E viscometer.

\* Typical physical values of Epol (from a technical data sheet)

Hydroxy content (meq/g): 0.90

Viscosity (poises/30°C): 700

Average molecular weight (VPO measurement): 2,500.

(Production Example 4)

5           An acrylic ester monomer solution in toluene composed of  
115.72 g of n-butyl acrylate, 60.00 g of methyl methacrylate,  
20.16 g of allyl methacrylate, 6.46 g of n-dodecylmercaptan,  
2.0 g of azobisisobutyronitrile and 400 mL of toluene was added  
dropwise from a dropping funnel over about 2 hours to a flask  
10 containing 50 mL of refluxing toluene in a nitrogen atmosphere.  
After completion of the dropping, the reaction was further  
allowed to proceed for 2 hours. The reaction mixture was  
evaporated and the residue was further dried at 80°C under  
reduced pressure for 3 hours to give about 195 g of a pale-yellow  
15 viscous liquid oligomer. The number of moles of allyl group  
as determined by iodometry was 0.0818 mol/100 g and the  
molecular weight as measured by VPO was 2,950, and thus it was  
found that about 2.4 allyl groups, on average, had been  
introduced into molecule.

20           (Production Example 5)

A round-bottomed flask equipped with stirring rod,  
thermometer, dropping funnel, nitrogen inlet tube and condenser  
was charged with 300 g (0.1 mol) of hydroxyl-terminated  
polycaprolactone (number average molecular weight: 3,000,  
25 hydroxyl equivalent: 1,500), 24.0 g of pyridine and 300 mL of  
THF and then 32 g of allyl chloroformate was gradually added  
dropwise from the dropping funnel at room temperature.  
Thereafter, the mixture was heated to 50°C and stirred for 3  
hours. The salt formed was filtered off, 150 mL of toluene was  
30 added to the filtrate, the mixture was washed with 200 mL of  
aqueous hydrochloric acid, then neutralized and concentrated  
to give allyl-terminated polycaprolactone. The oligomer had  
a number average molecular weight of 3,200 as determined by VPO  
measurement. From the olefin portion of a 300 MHz <sup>1</sup>H NMR  
35 spectrum, allyl group introduction could be confirmed. By



olefin quantitation by iodometry, it was confirmed that about 1.83 allyl-type unsaturated groups (0.0573 mol/100 g), on average, had been introduced into each molecule.

(Production Example 6)

5        An autoclave was charged with a solution of 0.02 g of zinc hexacyanocobaltate-glyme complex and 1.0 g of dipropylene glycol in THF and 4.8 g of propylene oxide, and the reaction was allowed to proceed at 76°C in a nitrogen atmosphere. Then, 72.6 g of propylene oxide was added to the reaction system. The  
10        unreacted monomer and solvent were recovered, and the residue was purified to give 75 g of an oil.

[0044]

      Upon GPC analysis, the product showed a single peak, and its hydroxyl value was 11.8 mg KOH/g. According to the  
15        procedure of Production Example 1, said product was reacted with NaOMe and then with allyl chloride to synthesize terminally allyl-etherified polyoxypropylene.

[0045]

[Effect of the Invention]

20        By adding, according to the present invention, various alkenyl-containing polymers to a polymerization system for living radical polymerization, it is possible to obtain, with ease, block copolymers resulting from binding of these various polymers to one another. Furthermore, since the block  
25        copolymer is polymerized by the living polymerization, block copolymers well controlled in the structure can be obtained.

30

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[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its subject to provide a method of easily producing a block copolymer composed of polymers having various main chains and a living radical polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] In the present invention, a block copolymer can be produced easily by adding various polymers (I) containing at least one alkenyl group to a living radical polymerization system. Furthermore, the block copolymer of the present invention has a characteristic for being well controlled in the structure.

[Selective Figure] none